(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 410 014 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
04.09.2013 Bulletin 2013/36

(51) Int Cl.:
C08L 61/14 (2006.01)
C08L 25/04 (2006.01)
C08L 51/04 (2006.01)
C08F 8/20 (2006.01)
C08L 55/02 (2006.01)
C08L 53/00 (2006.01)

(21) Application number: **11185887.4**

(22) Date of filing: **30.01.2009**

(54) Brominated polymers as flame retardant additives and polymer systems containing same

Bromierte Polymere als flammhemmende Zusatzstoffe und Polymersysteme damit

Polymères bromés comme additifs retardateurs de flamme, et système de polymères les contenant

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR

(30) Priority: **26.02.2008 US 31476 P**

(43) Date of publication of application:
25.01.2012 Bulletin 2012/04

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:
09714653.4 / 2 247 664

(73) Proprietor: **Dow Global Technologies LLC**
Midland, MI 48674 (US)

(72) Inventors:
- **King, Bruce A.**
  Midland, MI Michigan 48640 (US)
- **Worku, Anteneh**
  Pearland, TX Texas 77584 (US)
- **Stobby, William Gerald**
  Midland, MI Michigan 48640 (US)

(74) Representative: **Hull, John Philip**
Beck Greener
Fulwood House
12 Fulwood Place
London WC1V 6HR (GB)

(56) References cited:
WO-A-2007/019120

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to flame retardant additives for organic polymers, and in particular to brominated polymer flame retardant additives.

[0002] Flame suppressant (FR) additives are commonly added to polymer products used in construction and other applications. The presence of the FR additive allows the foam to pass standard fire tests, as are required in various jurisdictions. Various low molecular weight (<~1000 g/mol) brominated compounds are used as FR additives in these foam products. Many of these, such as hexabromocyclododecane, are under regulatory and public pressure that may lead to restrictions on their use, and so there is an incentive to find a replacement for them.

[0003] Various brominated materials have been suggested as FR additives. These include, for example, various brominated small molecules as well as certain brominated polymers. Among the brominated polymers that have been suggested are butadiene polymers and copolymers, brominated novolac resin allyl ethers, brominated poly (1,3-cycloalkadiene)s, and brominated poly (4-vinylphenol allyl ether)s. A number of such brominated small molecules and brominated polymers are described in WO 2007/019120.

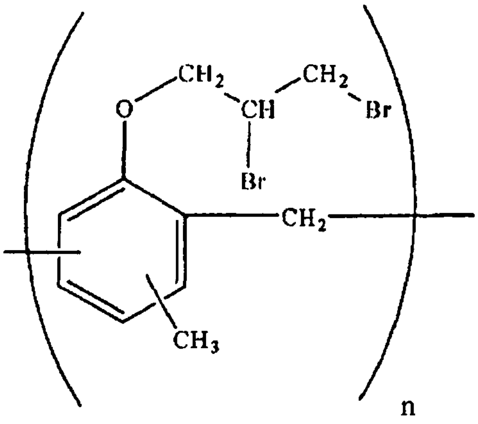
[0004] An alternative FR additive for extruded polymer foams should be capable of allowing the foam to pass standard fire tests, when incorporated into the foam at reasonably low levels. Because extruded foams are processed at elevated temperatures, it is important that the FR additive be thermally stable at the temperature conditions used in the extrusion process. For some foams, such as polystyrene and styrene copolymer foams, these temperatures are often 180°C or higher. Several problems are encountered if the FR additive decomposes during the extrusion process. These include loss of FR agent and therefore loss of FR properties, and the generation of decomposition products (such as HBr) that are often corrosive and therefore potentially dangerous to humans and harmful to operating equipment. The FR agent should not cause a significant loss of desirable physical properties in the polymer. It is preferable that the FR additive has low toxicity and is not highly bioavailable. A preferred type of blowing agent can be produced inexpensively from readily available starting materials.

[0005] WO 2007/019120 discloses styrenic polymer foams, especially expanded and/or extruded styrenic polymer foams, which are flame retarded by use of one or more flame retardant additives. These additives are i) a diether of tetrabromobisphenol-S, which ether groups do not contain bromine and wherein at least one of the ether groups is an allyl group; ii) a diether of tetrabromobisphenol-S, wherein at least one of the ether groups contains bromine; iii) a substituted benzene having a total of 6 substituents on the ring and wherein at least 3 of the substituents are bromine atoms and at least two of the substituents are C1-4 alkyl groups; iv) tribromoneopentyl alcohol; v) a tris(dibromoalkyl) benzenetricarboxylate in which each dibromoalkyl group contains, independently, 3 to 8 carbon atoms; vi) a brominated polybutadiene which is partially hydrogenated and/or aryl-terminated; vii) at least one brominated allyl ether of a novolac; viii) a brominated poly(1,3-cycloalkadiene); ix) a brominated poly(4-vinylphenol allyl ether); x) a brominated N,TSP-phenylenebismaleimide; xi) a brominated N,N'-(4,4'-methylenediphenyl)bismaleimide; xii) a brominated N, N'-ethylenebismaleimide; xiii) ethylenebis(dibromonorbornane-dicarboxamide); xiv) tetrabromobisphenol-A; or xv) a combination of any two or more of i) through xiv).

[0006] The present invention is in one aspect a polymer composition comprising a combustible polymer having mixed therein a brominated FR additive which is: a 2,3-dibromopropyl ether of a cresol novolac resin.

[0007] Brominated FR additives of the invention are readily prepared from starting polymers that are readily available and which in most cases are of low or moderate cost. These brominated FR additives are easily prepared from the starting polymers using straightforward chemistry. These FR additives in most cases have good thermal stability, and for that reason usually can be processed in polymer melt processing operations such as extrusion foaming. The FR additives are effective in imparting FR characteristics to combustible polymers, notably styrene polymers and copolymers, at reasonable levels of usage.

[0008] The flame retardant additive is a 2,3-dibromopropyl ether of a cresol novolac resin. It can be prepared from a cresol novolac starting resin, by sequentially reacting it with sodium hydride to form the corresponding phenoxide, then with allyl bromide to form the allyl ether, and then with a brominating agent. Flame retardant additives of this type include those having the idealized structure:



wherein n represents the degree of polymerization and the methyl substitution on the aromatic ring is preferably in the ortho or para position relative to the 2,3-dibromopropyl ether group.

[0009] Various bromination methods can be used to brominate the starting resins described above to produce the flame retardant additives. In some cases, the starting resin is conveniently brominated in a solvent using a source of elemental bromine as the brominating agent. The solvent is one which is not reactive with the polymer and which does not engage in free-radical reactions with the bromine source or bromine. Suitable solvents include, for example, carbon tetrachloride, dichloroethane, tetrahydrofuran, methylene chloride, methylene bromide, bromochloromethane (CH_2BrCl) and n-heptane. Suitable brominating conditions are well-known and described, for example, in McCutcheon, Org. Synth. Vol. 3, E.C. Horning, Ed., John Wiley and Sons, Inc. London 1955, pp. 526-528.

[0010] In another bromination approach, the starting resin is brominated using a quaternary ammonium tribromide as the brominating agent. Examples of suitable quaternary ammonium tribromides include phenyltrialkylammonium tribromide, a benzyltrialkylammonium tribromide or a tetraalkylammonium tribromide.

[0011] Starting resins containing epoxide groups can be brominated using lithium bromide or hydrogen bromide as a brominating agent.

[0012] Other techniques for brominating carbon-carbon unsaturation and epoxy groups as are known in the art are also useful.

[0013] The foregoing flame retardant additives may have a number average molecular weight of from about 500 to 250,000 or more, with a molecular weight of from about 1000 to 200,000, especially from 1500 to 100,000, being preferred. Molecular weight determinations for purposes of this invention are determined by gel permeation chromatography against polystyrene standards. The flame retardant additives preferably contain at least 10%, more preferably at least 20%, by weight bromine. The flame retardant additive may contain any greater amount of bromine, such as up to 80%, up to 70% or up to 55% by weight bromine

[0014] For most applications, preferred flame retardant additives of types i)-vi) have a glass transition temperature (Tg) of at least 35°C, preferably at least 50°C. Flame retardant additives having a lower glass transition temperature can be used, but they tend to be liquids or tacky solids, and for that reason are in some instances more difficult to handle and to mix with the combustible polymer. The flame retardant additive should have a glass transition temperature of no greater than 200°C, preferably no greater than 150°C, in order to facilitate melt-processing.

[0015] Flame retardant additives of the invention that have a glass transition temperature below 20°C, or even below 0°C, are most useful in suspension polymerization processes, particularly if they are soluble in the monomer or monomer mixture being polymerized. These low glass transition temperature additives tend to be liquids or pasty solids. They can be incorporated into a suspension polymerization process to make expandable polymer beads that contain the flame retardant additive, which then can be used to make bead foam. Higher T_g flame retardant additives that are soluble in the monomer or monomer mixture also can be used in suspension polymerization processes.

[0016] The flame retardant materials are useful as flame retardant additives for a variety of combustible polymers. "Combustible" here simply means that the polymer is capable of being burned. Combustible polymers of interest include polyolefins such as polyethylene (including copolymers of ethylene such as ethylene-α-olefin copolymers); polypropylene and the like; polycarbonates and blends of polycarbonates such as blends of a polycarbonate with a polyester, an acrylonitrile-styrene-butadiene resin or polystyrene; polyamides; polyesters; epoxy resins; polyurethanes; and polymers of vinyl aromatic monomers, as well as other flammable polymers in which the flame retardant additive can be dissolved or dispersed.

[0017] Polymers and copolymers of vinyl aromatic monomers are of particular interest as the combustible polymer. A "vinyl aromatic" monomer an aromatic compound having a polymerizable ethylenically unsaturated group bonded directly to a carbon atom of an aromatic ring. Vinyl aromatic monomers include unsubstituted materials such as styrene, divinylbenzene and vinyl naphthalene, as well as compounds that are substituted on the ethylenically unsaturated group (such as, for example alphamethylstyrene), and/or are ring-substituted. Ring-substituted vinyl aromatic monomers include those having halogen, alkoxyl, nitro or unsubstituted or substituted alkyl groups bonded directly to a carbon atom of an aromatic ring. Examples of such ring-substituted vinyl aromatic monomers include 2- or 4-bromostyrene, 2- or 4-chlorostyrene, 2- or 4-methoxystyrene, 2- or 4-nitrostyrene, 2- or 4-methylstyrene and 2,4-dimethylstyrene. Preferred vinyl aromatic monomers are styrene, alphamethyl styrene, 4-methyl styrene, divinylbenzene and mixtures thereof.

[0018] Especially preferred combustible polymers are polystyrene, styrene-acrylonitrile copolymers, styrene-acrylic acid copolymers and styrene-acrylonitrile-butadiene (ABS) resins. Polystyrene is an especially preferred combustible polymer.

[0019] Another combustible polymer of interest is a random, block or graft copolymer of butadiene and at least one vinyl aromatic monomer.

[0020] Expanded polymers of any of these types are of interest. An expanded combustible polymer suitably has a foam density of from about 1 to about 30 pounds per cubic foot (pcf) (16-480 kg/m^3), especially from about 1.2 to about 10 pcf (19.2 to 160 kg/m^3) and most preferably from about 1.2 to about 4 pcf (19.2 to 64 kg/m^3).

[0021] Flame retardant additives above having a 5% weight loss temperature of at least 180°C, preferably at least 200°C, as determined by the foregoing test, are preferred in making extruded foams, as their relatively good thermal stability allows them to be processed in the foam extrusion process by which the foam is made. 5% weight loss temperature is measured by thermogravimetric analysis as follows: ~10 milligrams of the flame retardant additive is analyzed using a TA Instruments model Hi-Res TGA 2950 or equivalent device, under a flow of gaseous nitrogen and a heating rate of 10°C/min over a range of from room temperature (nominally 25°C) to 600°C. The mass lost by the sample is monitored during the heating step, and the temperature at which the sample has lost 5% of its initial weight is designated the 5% weight loss temperature (5% WLT). This method provides a temperature at which a sample has undergone a cumulative weight loss of 5 wt%, based on initial sample weight. When used in conjunction with a combustible polymer that is to be melt-processed (either to blend it with the combustible polymer or to process the blend into an article such as a foam, extruded part, molded part, or the like), the flame retardant additive preferably exhibits a 5% WLT at least as high as the maximum temperature that the flame retardant additive will experience during the melt-processing operation.

[0022] Enough of the flame retardant additive above is incorporated into the combustible polymer to improve the performance of the combustible polymer in one or more standard fire tests. A suitable amount is typically at least one weight percent, or at least 2 weight percent or at least 3 weight percent, based on the weight of the polymer and the flame retardant additive. The amount of the flame retardant additive may be as much as 25 weight percent, or as much as 15 weight percent, or as much as 10 weight percent.

[0023] The amount of flame retardant that is used can alternatively (or in addition) be expressed in terms of the bromine content of the combustible polymer/flame retardant additive mixture. This bromine content in such a mixture is suitably at least 0.5 weight percent, more suitably at least 1.0 weight percent and even more suitably at least 1.5 weight percent, up to 20 weight percent, more suitably up to 10 weight percent and even more suitably up to 5 weight percent.

[0024] Any one or more of several tests can be used to indicate an improvement in FR performance. Suitable standardized tests include a limiting oxygen index (LOI) measurement, in accordance with ASTM D2863; and various time-to-extinguish tests or flame spread tests such as that known as FP-7 (described further below) and the DIN 4102 part 1, NF-P 92/501/4/5, SIA 183 or EN ISO 11925-2 tests which are used in Germany, France, Switzerland and Europe, respectively.

[0025] Improvement is established in the LOI method if the limiting oxygen index of the extruded polymer foam is increased by at least 0.5 unit, preferably by at least 1.0 unit and more preferably at least 2 units, compared to an otherwise like foam which does not contain an FR additive. FR performance in the LOI test may be increased by as much as 8 units or more. An extruded styrene polymer or copolymer foam containing a flame retardant additive of the invention may exhibit an LOI of at least 21%, preferably at least 22% and more preferably at least 24%.

[0026] Another fire test is a time-to-extinguish measurement, known as FP-7, which is determined according to the method described by A. R. Ingram in J. Appl. Poly. Sci. 1964, 8, 2485-2495. This test measures the time required for flames to become extinguished when a polymer sample is exposed to an igniting flame under specified conditions and the ignition source is then removed. An improvement in performance in this test is indicated by a shorter time being required for the flames to become extinguished. The time required for extinguishment under this test, when the polymer sample contains a flame retardant additive of the invention, is preferably reduced by at least one second, more preferably by at least 3 seconds and even more preferably by at least 5 seconds, compared to when the polymer sample does not contain an FR additive. A time to extinguishment on the FP-7 test is desirably less than 15 seconds, preferably less than 10 seconds and more preferably less than 5 seconds.

[0027] Improvement is indicated in other time-to-extinguishment or flame spread tests such as DIN 4102 part 1, NF-P 92/501/4/5, SIA 183 and EN ISO 11925-2 tests by a "pass" rating, or alternatively by a reduction in the flame height, flame extinction time and/or formation of burning droplets, as specified in the individual test methods, compared to a similar polymer sample that does not contain an FR additive.

[0028] Non-cellular polymers may perform differently than foamed polymers in these various tests. Similarly, particular flame retardant additives may provide a greater benefit in a non-cellular polymer system than in a cellular polymer, or vice-versa. Cellular polymers often present a more challenging problem than do non-cellular polymers, in part because of the higher surface area of the cellular polymers.

[0029] Polymer blends in accordance with the invention may include other additives such as other flame retardant additives, flame retardant adjuvants, thermal stabilizers, ultraviolet light stabilizers, nucleating agents, antioxidants, foaming agents, acid scavengers and coloring agents.

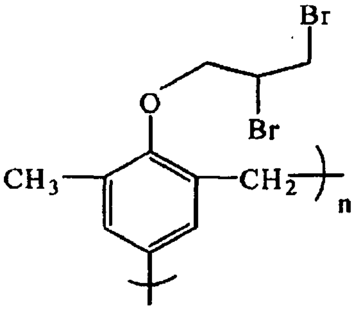
[0030] Polymer blends containing a flame retardant additive in accordance with the invention may be melt or solution processed to form a wide variety of products. Expanded (cellular) products are of interest because of their use in various building and automotive applications, in which fire performance is a concern. Expanded polymer products may have a bulk density of 10 pcf or less, more typically from 1.5 to 5 pcf and especially from 1.5 to 3 pcf. Expanded polymers of vinyl aromatic polymers, butadiene polymers and copolymers of vinyl aromatic polymers and/or butadiene polymers, as described before, are of particular interest. The expanded polymers may be used, for example, as insulating and/or cushioning materials in construction, household, automotive and other applications. Expanded polymers of the invention can also be used as an attached cushion or underlayment for carpeting. Non-cellular polymers can also be made in accordance with the invention.

[0031] The following example is provided to illustrate the invention, but not to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

[0032] Example

[0033] An o-cresol novolac resin (9.8 g, 0.082 mol) and DMF (70 mL) are added under nitrogen to a 250 ml 3-neck flask. NaH (2.55 g, 0.106 mol) is slowly added to the stirred solution. Allyl bromide (14.9 g, 0.123 mol) is then added drop-wise over 30 minutes. The reaction is continued for 19 hours at room temperature. The solids are filtered off and 70 mL toluene is added. The resulting solution is washed with 70 mL of water. The product allyl ether of the o-cresol novolac resin is isolated by evaporating off toluene, then drying overnight in vacuum oven at 60°C.

[0034] The o-cresol novolac allyl ether (5.95 g, 0.037 mol double bond) is dissolved in dichloroethane (DCE, 30 mL). Tetraethylammonium bromide (TEAB, 9.75 g, 0.046 mol) and DCE (25 ml) and then bromine (5.9 g, 0.037 mol) are added to a separate bottle. The resulting tetraethylammonium tribromide (TEATB) solution is then added slowly to the o-cresol novolac allyl ether solution. After 6 hours reaction at room temperature, solids are filtered off and rinsed with 20 mL DCE. The resulting polymer solution is washed with 25 mL water containing 0.5 g sodium bisulfite, then 25 mL water containing 0.1 g sodium bicarbonate. The resulting brominated polymer is isolated by evaporation of DCE, then dried overnight at 60°C in a vacuum oven. Yield is 9 g. The brominated polymer has a 5% WLT of 274°C and a Tg of 37°C. The brominated polymer contains 50.1% bromine and 380 ppm residual free bromide. It has the following idealized structure:



[0035] A blend of the brominated polymer in polystyrene (bromine content in the blend = 2.0 wt %) made and has an LOI of 23.7. The time to extinguishment in the FP-7 test is 1.9 s.

Claims

1. A polymer composition comprising a combustible polymer having mixed therein a brominated FR additive which is:

   a 2,3-dibromopropyl ether of a cresol novolac resin.

2. The polymer composition of claim 1, wherein the combustible polymer is a polymer or copolymer of a vinyl aromatic monomer.

3. The polymer composition of claim 2, wherein the combustible polymer is a polymer or copolymer of styrene, alpha-methyl styrene, 4-methyl styrene, divinylbenzene or a mixture of any two or more thereof.

4. The polymer composition of claim 2, wherein the combustible polymer is polystyrene, a styrene-acrylonitrile copolymer, a styrene-acrylic acid copolymer or a styrene-acrylonitrile-butadiene resin.

5. The polymer composition of claim 2, wherein the combustible polymer is polystyrene.

6. The polymer composition of claim 2, wherein the combustible polymer is a random, block or graft copolymer of butadiene and at least one vinyl aromatic monomer.

7. The polymer composition of any of claims 1-6, which is a foam.

Patentansprüche

1. Eine Polymerzusammensetzung, beinhaltend ein brennbares Polymer, in das ein bromierter FR-Zusatzstoff eingemischt wurde, der Folgendes ist:

   ein 2,3-Dibrompropylether eines Kresol-Novolak-Harzes.

2. Polymerzusammensetzung gemäß Anspruch 1, wobei das brennbare Polymer ein Polymer oder Copolymer eines vinylaromatischen Monomers ist.

3. Polymerzusammensetzung gemäß Anspruch 2, wobei das brennbare Polymer ein Polymer oder Copolymer von Styren, Alpha-Methylstyren, 4-Methylstyren, Divinylbenzen oder einer Mischung von beliebigen zwei oder mehr davon ist.

4. Polymerzusammensetzung gemäß Anspruch 2, wobei das brennbare Polymer Polystyren, ein Styren-Acrylnitril-Copolymer, ein Styren-Acrylsäure-Copolymer oder ein Styren-Acrylnitril-Butadien-Harz ist.

5. Polymerzusammensetzung gemäß Anspruch 2, wobei das brennbare Polymer Polystyren ist.

6. Polymerzusammensetzung gemäß Anspruch 2, wobei das brennbare Polymer ein statistisches, Block- oder Pfropf-Copolymer von Butadien und minde-

stens einem vinylaromatischen Monomer ist.

7. Polymerzusammensetzung gemäß einem der Ansprüche 1-6, die ein Schaum ist.

Revendications

1. Une composition de polymère comprenant un polymère combustible dans lequel est mélangé un additif ignifuge (FR) bromé qui est :

un éther 2,3-dibromopropyl d'une résine novolaque crésolique.

2. La composition de polymère de la revendication 1, dans laquelle le polymère combustible est un polymère ou un copolymère d'un monomère aromatique vinylique.

3. La composition de polymère de la revendication 2, dans laquelle le polymère combustible est un polymère ou un copolymère de styrène, d'alpha-méthylstyrène, de 4-méthyl-styrène, de divinylbenzène ou d'un mélange de deux quelconques ou plus de ceux-ci.

4. La composition de polymère de la revendication 2, dans laquelle le polymère combustible est du polystyrène, un copolymère styrène-acrylonitrile, un copolymère styrène-acide acrylique ou une résine acrylonitrile butadiène styrène.

5. La composition de polymère de la revendication 2, dans laquelle le polymère combustible est du polystyrène.

6. La composition de polymère de la revendication 2, dans laquelle le polymère combustible est un copolymère aléatoire, séquencé ou greffé de butadiène et au moins un monomère aromatique vinylique.

7. La composition de polymère de n'importe lesquelles des revendications 1 à 6, laquelle est une mousse.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2007019120 A **[0003] [0005]**

Non-patent literature cited in the description

- **MCCUTCHEON.** Org. Synth. John Wiley and Sons, Inc, 1955, vol. 3, 526-528 **[0009]**
- **A. R. INGRAM.** *J. Appl. Poly. Sci.,* 1964, vol. 8, 2485-2495 **[0026]**